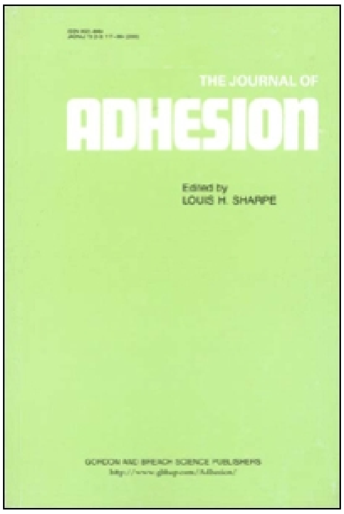

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Estimation of the Surface Energy of Polymer Solids

Toshio Hata[a]; Yasuaki Kitazaki[b]; Takanori Saito[c]
[a] Emeritus Professor of Tokyo Institute of Technology and Gunma University, Tokyo, Japan [b] Technical Department, Nichiban Co., Ltd. 100, Saitama, Japan [c] Research Laboratory of FSK Corporation, Saitama, Japan

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Estimation of the Surface Energy of Polymer Solids†

TOSHIO HATA

Emeritus Professor of Tokyo Institute of Technology and Gunma University. 8-1-7-103, Shakujii-machi, Nerima-ku, Tokyo 177, Japan

YASUAKI KITAZAKI

Technical Department, Nichiban Co., Ltd. 100, Nishihara Ohyazawa, Hidaka-cho, Iruma-gun, Saitama 350-12, Japan

TAKANORI SAITO

Research Laboratory of FSK Corporation. 5-14-42, Nishiki-cho, Warabi-shi, Saitama 335, Japan

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The methods to estimate the surface tension of polymer solids using contact angles have been reviewed in the first part. They are classified into the following three groups depending on the theories or the equations applied: (1) the methods using the Young's equation alone, (2) the methods using the combined equation of Young and Good-Girifalco, and (3) the methods using the equations of work of adhesion. Some notes and comments are given for each method and results are compared with each other. The two-liquids method for rather high energy surface is also introduced.

Next, some new possibilities to evaluate the surface tension of polymer solids are presented by our new contact angle theory in consideration of the friction between a liquid drop and a solid surface. The advancing and receding angles of contact (θ_a and θ_r) are explained by the frictional tension γ_F and accordingly two kinds of the critical surface tension $\gamma_C(\gamma_{Ca}$ and $\gamma_{Cr})$ are given.

This work has shown that one of the recommendable ways to evaluate γ_S is either the maximum $\gamma_{LV} \cos \theta_a$ or the maximum γ_C using the advancing contact angle θ_a alone, and another way is the arithmetic or the harmonic mean of the γ_{Ca} and γ_{Cr}. A

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depiction to determine the γ_C such as $\ln(1 + \cos\theta_0)$ *vs.* γ_{LV} with $\cos\theta_0 = (\cos\theta_a + \cos\theta_r)/2$ has also been proposed.

KEY WORDS Critical surface tension; contact angle; friction; methods; polymers; surface energy; surface tension; work of adhesion.

1 INTRODUCTION

The surface energy of polymer solids cannot directly be measured, but there recently appeared some indirect methods which include the extrapolating methods from liquid state using the temperature dependence or the molecular weight dependence of surface tension.

Another series of the method using the contact angle of liquids on a solid polymer surface has also been developed. There are varieties of this method depending on the theories or the equations applied, which will be reviewed in the first part of this paper. Next, we will present some possibilities to evaluate the surface tension of polymer solids from a new theory of the contact angle proposed by us.

2 THE REVIEW OF THE CONTACT ANGLE METHODS

Most of the contact angle methods are based on the Young's equation (1) concerning a liquid drop on an ideally smooth, undeformable, homogeneous and planar surface of a solid.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{1}$$

where γ_{SV} and γ_{LV} are surface tensions of the solid and the liquid respectively in equilibrium with the saturated vapor of the liquid, γ_{SL} the interfacial tension between the solid and the liquid and θ the contact angle. Equation (1) is rewritten as

$$\gamma_S = \gamma_{SL} + \gamma_{LV}\cos\theta + \pi_e \tag{2}$$

$$(\text{with } \pi_e = \gamma_S - \gamma_{SV})$$

$$\approx \gamma_{SL} + \gamma_{LV}\cos\theta \tag{3}$$

$$(\text{for negligible } \pi_e)$$

where γ_S is the surface tension of the solid in vacuum and π_e is the surface pressure. For a polymer of low surface energy, π_e can usually be neglected and Eq. (2) is approximated to the Eq. (3). Depending on the usage of the Young's equation whether alone or combined with the other surface-chemical equations the methods can be classified into following three groups.

2.1 The methods using Young's equation

(*a*) *The maximum* $\gamma_{LV} \cos\theta$ *(T. Hata and Y. Kitazaki*[1]*)*

In Eq. (2), if both γ_{SL} and π_e tend to zero, $\gamma_{LV}\cos\theta$ will get to the maximum and nearly be equal to γ_S. When liquids 1 and 2 have the equal polarity and chemical structure, the interfacial tension γ_{12} is experimentally known to be very small and close to zero. Similarly in the case of γ_{SL} between a solid and liquids, if one carefully chooses the testing liquids, one can find the condition that γ_{SL} is almost zero and π_e is so small that $\gamma_{LV}\cos\theta$ reaches the maximum giving γ_S. Figure 1 shows an example for polytrifluoroethylene.

The most important matter in this method is that one should use at least three kinds of testing liquids such as nonpolar, polar and hydrogen bonding liquids for a solid of unknown polarity. (More strictly speaking, acidic and basic liquid should be distinguished).

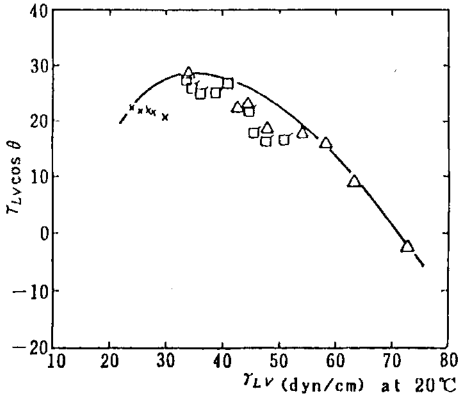

FIGURE 1 $\gamma_{LV}\cos\theta$ plotted against γ_{LV} at 20°C for Polytrifluoroethylene. (×) nonpolar liquids (*n*-alkanes), (△) polar liquids, (□) hydrogen-bonding liquids.

(*b*) *The maximum γ_C (Y. Kitazaki and T. Hata*[2]*)*

Equation (2) also shows that the extrapolated value of γ_{LV} at $\cos\theta = 1$ is equal to γ_S in case $\gamma_{SL} = 0$ and π_e is negligible. The critical surface tension γ_C of W. A. Zisman is defined as the γ_{LV} at $\cos\theta = 1$. Therefore, using the Eq. (2), γ_C is given by

$$\gamma_C = \gamma_S - \gamma_{SL}^{\circ} - \pi_e^{\circ} \tag{4}$$

where γ_{SL}° and π_e° are γ_{SL} and π_e at $\cos\theta = 1$, respectively. Since γ_{SL}° and π_e° depend on the combination of solid and liquid, γ_C may be diverse. Figure 2 shows the three different lines of $\cos\theta$ *vs.* γ_{LV} obtained by using liquid series of nonpolar (A), polar (B) and hydrogen bonding (C) for polytrifluoroethylene.

Zisman himself was interested in the minimum γ_C as a measure of the wetting property of the solid. However, we take an interest in the maximum γ_C, which is almost equal to γ_S because it corresponds to the minimum of $(\gamma_{SL}^{\circ} + \pi_e^{\circ})$.

In this method it is also necessary to use at least three kinds of testing liquids as above mentioned for an unknown specimen. If one does not like the discrete spectra as shown in Figure 2, one can use the band spectrum (assembly of plots) obtained from many liquids

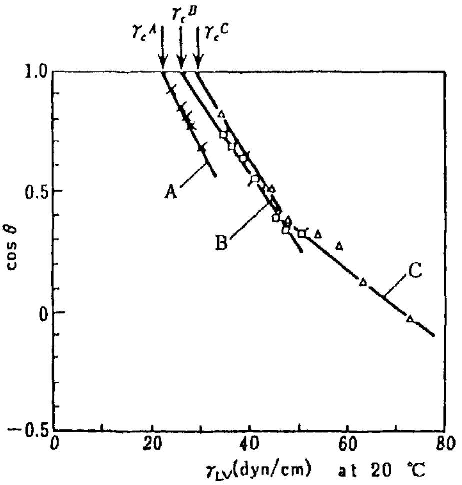

FIGURE 2 Zisman's plots using liquid series of different polarities for Polytrifluoroethylene. A: nonpolar liquids, B: polar liquids, C: hydrogen-bonding liquids.

having various polarities. The extremely right-hand line of the band give γ_C(max).

2.2 The methods using the combined equation of Young and Good-Girifalco

The interfacial tension γ_{12} has been expressed by the equations involving surface tension of each phase γ_1 and γ_2. One of them is the following equation of Good and Girifalco[3].

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi(\gamma_1\gamma_2)^{1/2} \tag{5}$$

where Φ is the parameter of molecular interaction. Combining this with the Young's equation gives

$$\gamma_S = \frac{\{\gamma_{LV}(1+\cos\theta)+\pi_e\}^2}{4\Phi^2\gamma_{LV}} \tag{6}$$

$$\approx \frac{\gamma_{LV}(1+\cos\theta)^2}{4\Phi^2} \tag{7}$$

or

$$\cos\theta = 2\Phi\left(\frac{\gamma_S}{\gamma_{LV}}\right)^{1/2} - 1 - \frac{\pi_e}{\gamma_{LV}} \tag{8}$$

$$\approx 2\Phi\left(\frac{\gamma_S}{\gamma_{LV}}\right)^{1/2} - 1 \tag{9}$$

If the value of Φ is found for a pair of the testing specimen and liquid, we can evaluate the approximate γ_S from the contact angle data using Eq. (7). Good and Girifalco[4] evaluated γ_S of a glassy fluorocarbon in this way, where they obtained Φ from the experimental values of γ_1, γ_2 and γ_{12} using Eq. (5) for a liquid homolog of the solid specimen and the testing liquid. However, this method is not general and the following methods using only the contact angle have instead been developed.

(*a*) *The method of S. Wu*[5]

According to the definition of γ_C, that is $\gamma_C = \lim_{\theta\to 0}\gamma_{LV}$, Wu derived the following relation from the Eq. (6)

$$\gamma_C = \Phi^2\gamma_S - \pi_e \tag{10}$$

where the higher terms are truncated in the series expansion.

Equation (10) shows that γ_C is a function of Φ, therefore Wu has used $\gamma_{C\phi}$ in place of γ_C. Combining the Eqs. (10) and (6), and neglecting the smaller terms gives

$$\gamma_{C\phi} = \frac{\gamma_{LV}(1+\cos\theta)^2}{4} \tag{11}$$

The maximum value of $\gamma_{C\phi}$ on the plot of $\gamma_{C\phi}$ *vs.* γ_{LV} is regarded as γ_S, because it corresponds to $\Phi_{\max} = 1$ in Eq. (10), when π_e can be neglected (Figure 3).

The criterion of $\gamma_C(\max) \approx \gamma_S$ has been proposed by us as mentioned in the Section 2.1(b).

If, otherwise, $\Phi_{\max} = 1$ could be considered to the condition of determining γ_S, then Wu may have gone a roundabout way through γ_C, because Eq. (6) directly gives

$$\gamma_S\Phi^2 = \frac{\gamma_{LV}(1+\cos\theta)^2}{4} + \pi_e\left(\frac{1+\cos\theta}{2} + \frac{\pi_e}{4\gamma_{LV}}\right) \tag{12}$$

$$\approx \frac{\gamma_{LV}(1+\cos\theta)^2}{4} + \pi_e \tag{13}$$

or the Eq. (7) gives

$$\gamma_S\Phi^2 \approx \frac{\gamma_{LV}(1+\cos\theta)^2}{4} \tag{14}$$

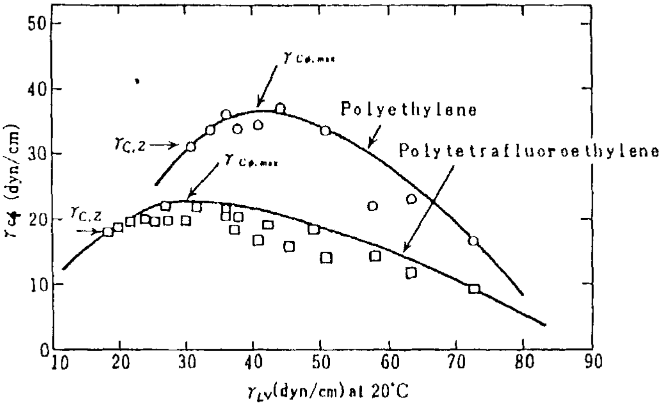

FIGURE 3 $\gamma_{C\phi} = ((1/4)\gamma_{LV}(1+\cos\theta)^2)$ plotted against γ_{LV} for polyethylene and polytetrafluoroethylene (after S. Wu, Ref. 5). $\gamma_{C,z}$ is the Zisman's γ_C.

Equation (13) is quite the same as the combined Eqs. (10) and (11). Neglecting π_e, the maximum value of $(1/4)\gamma_{LV}(1+\cos\theta)^2$ is here again corresponding to $\Phi_{\max}=1$ and gives γ_S.

(*b*) *The method of T. Hata and Y. Kitazaki*[1]

As Wu pointed out, $\Phi_{\max}$ may be 1 for a pair of equal polarity. This fact can be shown by the Good–Girifalco equation itself. Putting $\gamma_{12}=0$ as the condition of equal polarity, Eq. (5) gives $\Phi=(\gamma_1+\gamma_2)/2(\gamma_1\gamma_2)^{1/2}$. This is the ratio of the arithmetic mean to the geometric mean of γ_1 and γ_2, then if γ_1 does not differ too much from γ_2, Φ is nearly equal to unity. For example Φ is equal to 1.04 for even such different surface tensions as $\gamma_1=36$ and $\gamma_2=64$. Among many combinations of a solid with testing liquids, a certain one will satisfy the condition of $\Phi_{\max}=1$. To find this point there are two ways. The one is the same plot as made by Wu, but on the different basis of Eq. (13) or (14). The other is the plot of $\cos\theta$ against $1/(\gamma_{LV})^{1/2}$ according to Eq. (8). An example is shown in Figure 4 for polytetrafluoroethylene (PTFE) using Zisman's data.[6] The largest slope of the line through $(-1,0)$ approximately corresponds to $\Phi_{\max}=1$ and gives $2(\gamma_S)^{1/2}$. Otherwise, the intercept of the horizontal line at $\cos\theta=1$ by this largest slope gives $1/(\gamma_{LV})^{1/2}=1/(\gamma_S)^{1/2}$. We obtained from this method $\gamma_S=22.0$ dyn/cm for PTFE, the value being in good agreement with the value by other methods.

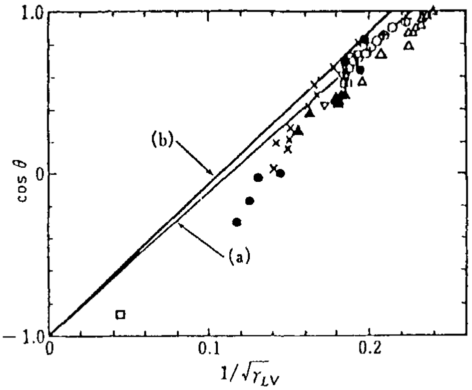

FIGURE 4 Plots of $\cos\theta$ *vs.* $1/(\gamma_{LV})^{1/2}$ for polytetrafluoroethylene after Zisman's data (Ref. 7). (a) The slope by Good and Girifalco. (b) The largest slope by Hata and Kitazaki.

2.3 The methods using the equations for the work of adhesion

This method starts from the fact that the surface tension γ can be divided into its components, γ^d, γ^p and if necessary γ^h, that is $\gamma = \gamma^d + \gamma^p (+\gamma^h)$, where the superscripts d, p and h refer to dispersion (nonpolar), polar and hydrogen bonding components. If these components are determined independently, we can obtain γ_S by summing them up. On the other hand, the work of adhesion W_a has been expressed by these components of two phases, which originated in the work of F. M. Fowkes[7] for non-polar liquids as

$$W_a = 2(\gamma_1^d \gamma_2^d)^{1/2} \tag{15}$$

This has been extended to a pair of polar liquids as follows;

Y. Kitazaki and T. Hata[8]

$$W_a = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} + 2(\gamma_1^h \gamma_2^h)^{1/2} \tag{16}$$

D. K. Owens, *et al.*[9] D. H. Kaelble, *et al.*[10]

$$W_a = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} \tag{17}$$

Instead of these equations of geometric mean, the harmonic mean equation has been proposed by S. Wu,[11] that is

$$W_a = \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \tag{18}$$

Combining any of these equations with the Young-Duprè equation,

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} = \gamma_{LV}(1 + \cos\theta) \tag{19}$$

the following equation is reached from, for example, the equation (17)

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_S^d \gamma_L^d)^{1/2} + 2(\gamma_S^p \gamma_L^p)^{1/2} \tag{20}$$

Using at least two kinds of liquids with known γ_L^d and γ_L^p, γ_S^d and γ_S^p are determined from the contact angle measurements and then γ_S.

2.4 The two-liquids method[12]

The contact angle method above described cannot be applied to a solid of such high energy surface that most of liquids never form beads but spontaneously spread out. Even in such cases, a liquid drop can be formed on the surface immersed in the second liquid which is incompatible with the first. For instance if a drop of *n*-alkane (H) is introduced on the surface of a solid (S) immersed in water (W), we have the following equations using the geometric mean for the work of adhesion.

$$\gamma_{SW} = \gamma_{SH} + \gamma_{HW} \cos\theta \tag{21}$$

$$\gamma_{SH} = \gamma_S + \gamma_H - 2(\gamma_S^d \gamma_H^d)^{1/2} \tag{22}$$

$$\gamma_{SW} = \gamma_S + \gamma_W - 2(\gamma_S^d \gamma_W^d)^{1/2} - 2(\gamma_S^p \gamma_W^p)^{1/2} \tag{23}$$

TABLE 1

The surface tension of polymer solids by various methods (dyn/cm) at 20°C

Polymer solids	γ_C (max) *1	$\gamma_{LV}\cos\theta$ (max)	γ_S (Φ_{max}) *2	$\gamma_{C\phi}$ (max)	γ_L (20°C) *3	G.M. (2) *4	G.M. (3) *5	H.M. *6
Polytetrafluoroethylene	21.5(B)	21.6	22.0	22.7	22.6^{J}	19.1	21.5	22.5
Polytrifluoroethylene	29.0(C)	28.4	28.7	28.7	—	23.9	31.2	27.3
Poly(vinylidene fluoride)	40.0(C)	37.1	37.0	37.2	—	30.3	40.2	33.2
Poly(vinyl fluoride)	44.2(C)	42.7	42.7	42.7	—	36.7	43.5	38.4
Polyethylene (air)^{*7}	38.3(B)	36.1	36.5	36.5	35.6	33.2	35.6	36.1
Polyethylene (glycerine)^{*7}	43.9(B)	43.1	43.1	43.1	(35.6)	—	43.3	—
Polyethylene (Hg)^{*7}	41.3(B)	39.4	39.5	39.5	(35.6)	—	41.6	—
Polyethylene (PTFE)^{*7}	29.2(B)	26.8	28.6	28.6	(35.6)	—	26.8	—
Polyethylene (treated by chromic acid)	52.0(B)	49.9	50.3	50.2	(35.6)	—	—	—
Polypropylene	29.8(B)	27.5	29.1	29.1	29.8	—	29.8	—
n-$C_{36}H_{74}$(cleavage surface)^{Z}	20.6(A)	21.5	21.8	22.0	35.0^{W}	19.1	20.6	23.6
Polystyrene^{Z}	43.0(B)	43.1	43.1	43.1	40.6	42.0	40.6	42.6
Poly(methyl methacrylate)	43.5(BC)	44.9	45.0	44.9	41.4^{W}	40.2	43.5	41.2
Poly(vinyl chloride)^{Z}	43.9(B)	43.8	43.9	43.8	—	41.5	44.0	41.9
Poly(vinylidene chloride)^{Z}	44.0(B)	44.4	44.4	44.6	—	45.0	45.8	45.4
Nylon 66^{Z}	46.0(C)	42.9	43.0	43.2	46.5^{W}	47.0	46.5	44.7
KEL-F^{Z}	31.5(B)	32.1	31.9	32.1	30.9^{S}	27.5	31.5	30.1
Polyoxymethylene	46.5(C)	44.6	44.5	44.7	—	—	44.6	—
Poly(ethylene terephthalate)	43.9(B)	43.8	43.9	43.8	44.6^{W}	41.3	—	42.1
PET(corona discharged)	51.1(C)	51.9	51.9	52.0	—	—	—	—
Poly(γ-methyl-L-glutamate)(α)^{Z,*8}	50.0(C)	—	—	—	—	—	48.0	—
Poly(γ-methyl-L-glutamate)(β)^{Z,*8}	37.0(BC)	—	—	—	—	—	37.8	—
Polyglycine^{Z}	48.5(C)	50.4	50.4	50.7	—	—	—	—
Bakelite	38.0(BC)	36.9	37.3	37.5	—	—	38.5	—

Notes: *1, A, B and C in the parenthesis mean that the nonpolar (A), polar (B) and hydrogen-bonding (C) liquid series each gave the maximum γ_C. *2. The calculated values from the largest slope of $\cos\theta$ *vs.* $1/(\gamma_{LV})^{1/2}$. *3. The extrapolated values of surface tension at 20°C from molten state. *4. The geometric mean equation of two components. *5. The geometric mean equation of three components. *6. The harmonic mean equation. *7. Surfaces produced by the contact with materials in parenthesis. *8. α and β mean the surface of α-helix conformation and β-structure, respectively. *Others Z, J, W and S mean that γ_S are calculated from the data of Zisman, Johnson, Wu and Schonhorn, respectively.

where γ_S, γ_H and γ_W are the surface tensions of solid, hydrocarbon and water and γ_{SW}, γ_{SH} and γ_{HW} are the interfacial tensions between S/W, S/H and H/W respectively. Combining the equations (21) ~ (23) we have

$$\underbrace{\gamma_H - \gamma_W - \gamma_{HW}\cos\theta}_{Y} = 2(\gamma_S^d)^{1/2}\underbrace{\{(\gamma_H^d)^{1/2} - (\gamma_W^d)^{1/2}\}}_{X} - 2(\gamma_S^p\gamma_W^p)^{1/2} \qquad (24)$$

By using a series of n-alkanes, a linear relationship is obtained by plotting the quantity Y as a function of X, and accordingly γ_S^d is given by the slope and γ_S^p by the intercept. L. Lavielle and J. Schultz[13] recently adopted this two-liquids method for the estimation of γ_S of acrylic acid grafted polyethylene.

This method has an advantage over the single liquid method in that the surface pressure π_e does not appear in the equations. However the adsorption of the second liquid may be a new problem.

Now, γ_S obtained by the various methods are summarized in Table I and especially γ_S of the fluorine substituted polyethylenes obtained by the two ways are shown in Figure 5 together with

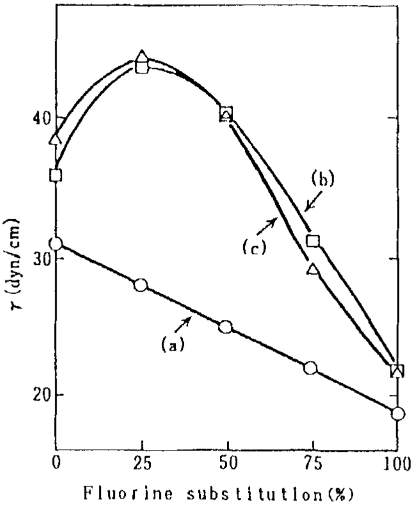

FIGURE 5 γ_S and Zisman's γ_C of fluorine substituted polyethylene, (a) Zisman's γ_C, (b) γ_S by the extended Fowkes Eq. (16), (c) γ_C(max).

Zisman's γ_C. The maximum γ_S of poly(vinylfluoride) is reasonable when taking its polarity into consideration.

In conclusion, we recommend the methods of the maximum $\gamma_{LV}\cos\theta$ and the maximum γ_C as described in the section 2.1, because they are simply based on the Young's equation, while the others are all combined with equations which are not thoroughly proved.

3 A NEW METHOD OF THE ESTIMATION OF γ_S USING CONTACT ANGLES

3.1 The contact angle in consideration of the friction between liquid drop and solid surface

The angle (θ) of contact between a liquid drop and a solid surface has been derived by us as follows,[14]

$$\cos\theta = \frac{r}{\gamma_{LV}}\{\gamma_S - \gamma_{SL} - \pi_e \pm \gamma_F\} \qquad (25)$$

where r is the roughness factor and γ_F the frictional tension defined by

$$\gamma_F = \left(\frac{\tau}{\sigma_Y} + \tan\alpha\right)\left(\frac{mg\sigma_Y\cos\theta}{\pi}\right)^{1/2} \qquad (26)$$

with τ as the shear stress at liquid-solid interface, σ_Y the yield stress of the liquid, α the base angle of isosceles triangle expressing surface roughness, r the roughness factor being equal to $1/\cos\alpha$, and mg the weight of the liquid drop.

The plus and minus signs before γ_F correspond to the receding angle θ_r and the advancing angle θ_a of contact, respectively. Our theoretical Eq. (25) is in result the form of the equation of Adam and Jessop[15] who *a priori* introduced the friction force. According to our previous work[16] the reversible and the irreversible work of adhesion, W_a and W_A, for a partially miscible interface can be expressed by and related with each other as,

$$W_a = \gamma_S + \gamma_{LV} - \gamma_{SL} = 2(\gamma_S)^{\psi_S}\gamma_L)^{\psi_L} \qquad (27)$$

$$W_A = \frac{\pi}{2}(\tan\delta_S)^{\psi_S}(\tan\delta_L)^{\psi_L}W_a \qquad (28)$$

where $\tan\delta_S$ and $\tan\delta_L$ are the loss tangent of the solid and the liquid, $\psi_S = (1-\psi_L)$ and ψ_L are the mean mole fraction of the molecule or the segment of the solid and the liquid in the interfacial layer.

Taking the irreversibility of the friction into account,[14] W_A can be equated to γ_F for the flat surface ($r = 1$). By substituting the Eq. (28) for the γ_F in the Eq. (25), we obtain the following equation for the flat surface

$$\cos\theta = \frac{\gamma_S - \gamma_{SL} - \pi_e}{\gamma_{LV}} \pm \pi\left(\frac{\gamma_S}{\gamma_{LV}}\right)^{\psi_S}(\tan\delta_S)^{\psi_S}(\tan\delta_L)^{\psi_L} \qquad (29)$$

Eliminating $(\gamma_S - \gamma_{SL})$ in the equation (29) by the Eq. (27) gives

$$\cos\theta = \left\{2\left(\frac{\gamma_S}{\gamma_{LV}}\right)^{\psi_S}\left[1 \pm \frac{\pi}{2}(\tan\delta_S)^{\psi_S}(\tan\delta_L)^{\psi_L}\right] - 1\right\} - \frac{\pi_e}{\gamma_{LV}} \qquad (30)$$

Incidentally, the equations (29) and (30) prove the positive correlation of the advancing contact angle and $\tan\delta_S$ which was experimentally shown by Neumann and Tanner[17].

3.2 The critical surface tension γ_C and the surface tension of solid

3.2.1 *Relationship of γ_C with the advancing angle θ_a or the receding angle θ_r of contact*

As the Eq. (25) shows, the critical surface tension γ_C depends on whether the contact angle is advancing or receding, then two kinds of the γ_C, *i.e.*, γ_{Ca} for θ_a and γ_{Cr} for θ_r can be obtained by making θ be zero in the Eq. (25),

$$\gamma_{Ca} = r(\gamma_S - \gamma_{SL}^{\circ} - \pi_e^{\circ} - \gamma_F^{\circ}) = r(\gamma_{SV}^{\circ} - \gamma_{SL}^{\circ} - \gamma_F^{\circ}) \qquad (31)$$

$$\gamma_{Cr} = r(\gamma_S - \gamma_{SL}^{\circ} - \pi_e^{\circ} + \gamma_F^{\circ}) = r(\gamma_{SV}^{\circ} - \gamma_{SL}^{\circ} + \gamma_F^{\circ}) \qquad (32)$$

where the superscript (°) stands for the corresponding quantity at the zero contact angle. The equations (31) and (32) indicate the following.

a) The difference between γ_{Ca} and γ_{Cr} arises from the frictional tension, and the inequality or the difference of them can be written as

$$\gamma_{Ca} < r(\gamma_S - \gamma_{SL}^{\circ} - \pi_e^{\circ}) < \gamma_{Cr} \tag{33}$$

$$\gamma_{Cr} - \gamma_{Ca} = 2r\gamma_F^{\circ} \tag{34}$$

b) Since the $\gamma_C(\gamma_{Ca}, \gamma_{Cr})$ is a function of such factors as π_e°, γ_{SL}° and γ_F° along with γ_S and r, the γ_C of the solid has diversity due to those factors depending on the liquids used for measuring the contact angle.

c) According to the reason above mentioned, experimental values and/or the information on π_e°, γ_{SL}°, γ_F and r as well as γ_{Ca} and γ_{Cr} are needed in order to estimate the γ_S from the γ_C.

3.2.2 *Estimation of γ_S from γ_{Ca} and γ_{Cr}*

When estimating γ_S from γ_C, the γ_F can be eliminated by adding the Eqs. (31) to (32) as follows.

$$\gamma_S = \frac{\gamma_{Cr} + \gamma_{Ca}}{2r} + \gamma_{SL}^{\circ} + \pi_e^{\circ} \tag{35}$$

$$\approx \frac{\gamma_{Cr} + \gamma_{Ca}}{2} \quad \left(\text{for } r = 1,\ \gamma_{SL}^{\circ} + \pi_e^{\circ} \ll \frac{\gamma_{Cr} + \gamma_{Ca}}{2}\right) \tag{36}$$

If we assume here that γ_{SL}°, γ_{Ca} and γ_{Cr} are compatible with the Eq. (27), γ_{SL} can be expressed by

$$\gamma_{SL}^{\circ} = \gamma_S - \gamma_S^{\psi_S}(\gamma_{Cr}^{\psi_L} + \gamma_{Ca}^{\psi_L}) + \frac{\gamma_{Cr} + \gamma_{Ca}}{2} \tag{37}$$

Equation (35) can then be rearranged in case $\psi_s \neq 0$ as

$$\gamma_S = \left\{\frac{1}{\gamma_{Cr}^{\psi_L} + \gamma_{Ca}^{\psi_L}}\left[\frac{1}{2}\left(1 + \frac{1}{r}\right)(\gamma_{Cr} + \gamma_{Ca}) + \pi_e^{\circ}\right]\right\}^{1/\psi_S} \tag{38}$$

$$= \left(\frac{\gamma_{Cr} + \gamma_{Ca} + \pi_e^{\circ}}{\gamma_{Cr}^{\psi_L} + \gamma_{Ca}^{\psi_L}}\right)^{1/\psi_S} \quad \text{for} \quad r = 1 \tag{39}$$

$$= \left(\frac{\gamma_{Cr} + \gamma_{Ca}}{\gamma_{Cr}^{\psi_L} + \gamma_{Ca}^{\psi_L}}\right)^{1/\psi_S} \quad \text{for} \quad \pi_e/(\gamma_{Cr} + \gamma_{Ca}) \ll 1 \tag{40}$$

In case $\psi_S = 1$, Eq. (38) is reduced to

$$\gamma_S \approx \frac{\gamma_{Cr} + \gamma_{Ca}}{2} \quad \text{for} \quad r = 1, \qquad \pi_e/(\gamma_{Cr} + \gamma_{Ca}) \ll 1 \tag{41}$$

For the macroscopically flat surface, we can estimate γ_S from Eq.

(30) under the condition of $\psi_S \neq 0$ as

$$\gamma_S = \left\{ \frac{2 + \frac{\pi_e^{\circ}}{2}\left(\frac{1}{\gamma_{Cr}} + \frac{1}{\gamma_{Ca}}\right)}{\left(\frac{1}{\gamma_{Cr}}\right)^{\psi_S} + \left(\frac{1}{\gamma_{Ca}}\right)^{\psi_S}} \right\}^{1/\psi_S} \tag{42}$$

$$\approx \left\{ \frac{2}{\left(\frac{1}{\gamma_{Cr}}\right)^{\psi_S} + \left(\frac{1}{\gamma_{Ca}}\right)^{\psi_S}} \right\}^{1/\psi_S} \quad \text{for} \quad \frac{\pi_e^{\circ}}{4}\left(\frac{1}{\gamma_{Cr}} + \frac{1}{\gamma_{Ca}}\right) \ll 1 \tag{43}$$

When ψ_S is unity, the Eq. (42) can be reduced to

$$\gamma_S = \frac{2\gamma_{Cr}\gamma_{Ca}}{\gamma_{Cr} + \gamma_{Ca}} + \frac{\pi_e^{\circ}}{2} \tag{44}$$

While the Eq. (30) provides us with the following equations for $\psi_s \neq 0$

$$\gamma_S = \gamma_{Ca} \left\{ \frac{1 + \frac{\pi_e^{\circ}}{2\gamma_{Ca}}}{1 - \frac{\pi}{2}(\tan \delta_S)^{\psi_S}(\tan \delta_L)^{\psi_L}} \right\}^{1/\psi_S} \tag{45}$$

$$\gamma_S = \gamma_{Cr} \left\{ \frac{1 + \frac{\pi_e^{\circ}}{2\gamma_{Cr}}}{1 + \frac{\pi}{2}(\tan \delta_S)^{\psi_S}(\tan \delta_L)^{\psi_L}} \right\}^{1/\psi_S} \tag{46}$$

If the γ_F is small enough compared to the reversible work of adhesion W_a i.e.,

$$\frac{\gamma_F}{W_a} = \frac{\pi}{2}(\tan \delta_S)^{\psi_S}(\tan \delta_L)^{\psi_L} \ll 1 \tag{47}$$

and π_e is negligible, i.e.,

$$\frac{\pi_e^{\circ}}{2\gamma_C} \ll 1 \tag{48}$$

Equations (45) and (46) can be reduced as

$$\gamma_S = \gamma_{Ca}\left(1 + \frac{\pi_e^\circ}{2\psi_S \gamma_{Ca}}\right)\left\{1 + \frac{\pi}{2\psi_S}(\tan \delta_S)^{\psi_S}(\tan \delta_L)^{\psi_L}\right\} \quad (49)$$

$$\gamma_S = \gamma_{Cr}\left(1 + \frac{\pi_e^\circ}{2\psi_S \gamma_{Cr}}\right)\left\{1 - \frac{\pi}{2\psi_S}(\tan \delta_S)^{\psi_S}(\tan \delta_L)^{\psi_L}\right\} \quad (50)$$

In the case of $\psi_S = 0$, we obtain the following from Eq. (29).

$$\gamma_S = \gamma_{Ca}\left(1 + \frac{\pi_e^\circ}{\gamma_{Ca}} + \tan \delta_L\right) + \gamma_{SL}^\circ \quad (51)$$

$$\gamma_S = \gamma_{Cr}\left(1 + \frac{\pi_e^\circ}{\gamma_{Cr}} - \tan \delta_L\right) + \gamma_{SL}^\circ \quad (52)$$

Equations (51) and (52) can be rewritten as

$$\gamma_S = \gamma_C + \gamma_{SL}^\circ \quad \text{for} \quad \frac{\pi_e^\circ}{\gamma_C} \pm \tan \delta_L \ll 1 \quad (53)$$

where the γ_C is the γ_{Ca} or the γ_{Cr}. Equation (53) is identical to Eq. (4) derived by the Young's relationship.

3.2.3 *Estimation of the mean mole fraction ψ_S*

In the case that γ_F is small enough as shown in the Eq. (47), and π_e/γ_{LV} is negligibly small, Eq. (30) can be reduced to

$$\cos \theta \approx 2\left(\frac{\gamma_S}{\gamma_{LV}}\right)^{\psi_S} - 1 \quad (54)$$

We then obtain the following equation.

$$\ln(1 + \cos \theta) \approx \ln 2\,(\gamma_S)^{\psi_S} - \psi_S \ln \gamma_{LV} \quad (55)$$

which shows an approximate ψ_S is able to be determined by the slope in the plot of $\ln(1 + \cos \theta)$ *vs.* $\ln \gamma_{LV}$, and the γ_C can also be determined by the γ_{LV} corresponding to the intersection of $\ln 2$ and $\ln \gamma_{LV}$.

3.3. Comparison of γ_S determined by various methods

Using the data on γ_{Cr} and γ_{Ca} by Petke and Ray[18], we can estimate the γ_S of some polymers. Besides, Zisman's[6] and our

TABLE II
Estimation of γ_S of polymers from γ_{Ca} and γ_{Cr} reported.

Polymers	*1 γ_{Cr}	*1 γ_{Ca}	*2 γ_S Eq. (36)	*2 γ_S Eq. (44)	γ_S $\gamma_{LV}\cos\theta$ (max)	*3 ψ_S Eq. (55)	*3 γ_S Eq. (55)	*4 γ_S Eq. (40)	*4 γ_S Eq. (43)
PE	42.8^{a}	36.3^{a}	39.6	39.3	36.1	0.844	39.4	39.6	39.3
PS	40.7^{a}	33.3^{a}	37.0	36.6	43.1	0.577	42.7	37.1	36.7
POM	43.3^{a}	38.2^{a}	40.8	40.6	44.6	0.847	43.7	40.8	40.6
PC	43.5^{a}	34.7^{a}	39.1	38.6	32.0	0.683	35.3	39.2	38.7
PET	45.5^{a}	40.3^{a}	42.9	42.7	43.8	0.914	44.1	42.9	42.7
FEP	24.0^{a}	19.8^{a}	21.9	21.7					
PTFE	20.0^{b}	7.6^{b}	14.0	11.1	21.6	0.679	23.1	14.5	11.5
PMMA	45.6^{b}	44.0^{b}	44.8	44.8	45.0	1.02	43.4	44.7	44.7

*1. At 20°C after Petke and Ray[18]; b) at 25.5 ± 1.5°C after Shimi and Goddard[19].

*2. After the data*1.

*3. Estimated by Eq. (55) with our data of θ_a at 20 ± 2°C.

*4. γ_{Ca}, γ_{Cr}, and ψ_S at 20°C after Petke and Ray[18], and at 25.5 ± 1.5°C after Shimi and Goddard[19] using Eq. (55).

works allow us to estimate the ψ_S and the γ_{Ca} from the Eq. (55). Results are summarized in Table II, which indicates that each method using γ_{Ca} and γ_{Cr} is able to give reasonable γ_S being almost equal to, for example, the maximum $\gamma_{LV} \cos \theta$. So we consequently recommend rather the simplified Eqs. (36) and (44) than equations involving the ψ_S and ψ_L.

4 CONCLUDING REMARKS

In this article we have reviewed and proposed various methods to evaluate γ_S of polymers, above all using contact angles. The following methods are eventually recommended as mentioned in the text.

1) Either the maximum $\gamma_{LV} \cos \theta$ or the maximum γ_C using the advancing contact angle is appropriate to estimate the γ_S.

2) Allowing for the frictional tension at the liquid-solid interface, both the critical surface tension γ_{Ca} and γ_{Cr} should be determined by advancing angle (θ_a) and receding angle (θ_r) of contact, respectively. The γ_S can then be obtained from the arithmetic mean (Eq. (36)) or the harmonic mean (Eq. (44)) of γ_{Ca} and γ_{Cr}.

3) Another recommendable method is based on the contact angle (θ_0) being independent of the frictional tension γ_F. An equation

about $\cos \theta_0$ can readily be derived by the equation (25) as follows.

$$\cos \theta_0 = \frac{\cos \theta_a + \cos \theta_r}{2} \tag{56}$$

Therefore γ_S can also be evaluated from a plot such as $\gamma_{LV} \cos \theta_0$ *vs.* γ_{LV} (*e.g.*, Fig. 1), $\cos \theta_0$ *vs.* γ_{LV} (the Zisman's plot) or $\ln(1 + \cos \theta_0)$ *vs.* $\ln \gamma_{LV}$(Eq. (55)).

Finally, we just touch on the mean mole fraction ψ_S and ψ_L at the liquid-solid interface. The estimated values of $\psi_S = (1 - \psi_L)$ is diverse and not necessarily equal to 0.5 as shown in the Table 2. This result shows that the Berthelot's approximation ($\psi_S = \psi_L = 0.5$) is not appropriate for evaluating the work of adhesion, the critical surface tension and other quantities affected by the interaction in the intermixing interface. The divergence of ψ_S from 0.5 has also been confirmed by the Eq. (27) using directly measured γ_1, γ_2, and γ_{12} of liquids. This is an important fact in surface-chemical problems.

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